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(54) **ORGANIC ELECTROLUMINESCENCE DEVICE**

(57) An organic electroluminescence device which comprises a pair of electrodes comprising an anode and a cathode and a layer of organic compounds comprising at least an organic light emitting layer and disposed between the pair of electrodes, wherein the layer of organic compounds comprises a light emitting material and a

bis-condensed aromatic cyclic compound. The organic electroluminescence device exhibits suppressed crystallization in driving for a long time or in environments at high temperatures, has improved durability and is advantageously used in practical applications.

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layer and disposed between the pair of electrodes, wherein the layer of ~~organic compound~~ comprises a ~~single~~ material and a bis-condensed aromatic cyclic compound.

THE MOST PREFERRED EMBODIMENT TO CARRY OUT THE INVENTION

[illegible]

[0012] It is preferable that the light emitting material is a compound represented by the following general formula:



wherein X and Y each independently represent a substituted or unsubstituted group having 6 to 58 carbons or a substituted or unsubstituted monovalent heterocyclic group having 3 to 58 carbon atoms, and Ar represents same group or different groups and Ar represents an arylene group having 6 to 58 carbon atoms, a polycyclic or a divalent triphenylamine residue group, a divalent heterocyclic group having 3 to 58 carbon atoms or a divalent group formed by bonding these groups to each other.

[0013] Examples of the substituent in the groups represented by X and Y include hydrogen atoms, cyano group, nitro group, alkyl groups, alkoxy groups, aryloxy groups, aryl groups, heteroaryl groups, monocyclic groups, condensed polycyclic groups, arylsilyl groups,

[0014] The compound represented by general formula (1) may be used as a

[0015] The bis-condensed aromatic cyclic compound described above is used as a material for the light emitting layer in the light emitting layer without adverse effects on the light emitting property of the light emitting layer in driving at high temperatures and the storage property by mixing the bis-condensed aromatic cyclic compound is suitable as the material for the light emitting layer.

[0016] The above bis-condensed aromatic cyclic compound is a compound composed of two or more aromatic rings to each other through a linking group or a single bond. As the condensed aromatic cyclic compound, naphthalene, anthracene, fluorene, perylene, pyrene, phenanthrene, triphenylene, tetracene, pentacene, triphenylene, rubicene, pycene, coronene and fluoranthene are preferable, and naphthalene, anthracene, fluorene, perylene, pyrene, phenanthrene and fluoranthene are more preferable. As the hydrocarbon group, arylene groups are preferable. In particular, the phenylene compound is preferable as the bis-condensed aromatic cyclic compound.

[0017] In the bis-condensed aromatic cyclic compound, the plane of one aromatic ring is twisted relative to that of the other aromatic ring. Since the angle between the planes is not fixed to a specific value, the compound does not have a specific stable configuration with the molecule of the light emitting material. Therefore, when the molecules of the emitting material move so as to be arranged in a specific manner, the compound does not have a great effect of suppressing the movement. Since the angle between the planes of the rings in the bis-condensed aromatic cyclic compound is fixed to a specific value, the molecules of the compound are not arranged in a specific manner and crystallization does not take place.

[0018] As the bis-condensed aromatic cyclic compound, a compound represented by general formula (2) or general formula (3) is preferable:

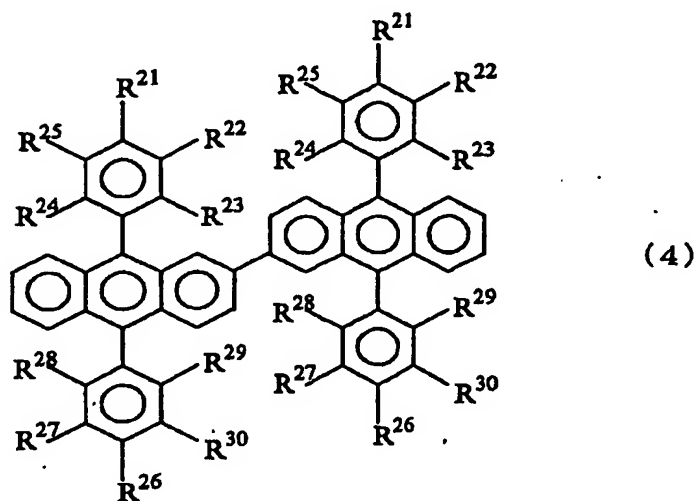
aromatic heterocyclic group having 2 to 30 carbon atoms, a substituted or unsubstituted aralkyl group having 7 to 30 carbon atoms, a substituted or unsubstituted aryloxy group having 6 to 30 carbon atoms, a substituted or unsubstituted alkoxycarbonyl group having 1 to 30 carbon atoms or carboxyl group.

[0019] Examples of the substituent in the groups in above general formulae (2) and (3) include halogen atoms, cyano group, nitro group, alkyl groups, alkoxy groups, aryloxy groups, alkylthio group, arylthio groups, arylalkyl groups, monocyclic groups, condensed polycyclic groups, arylsilyl groups, heterocyclic groups and alkenyl groups.

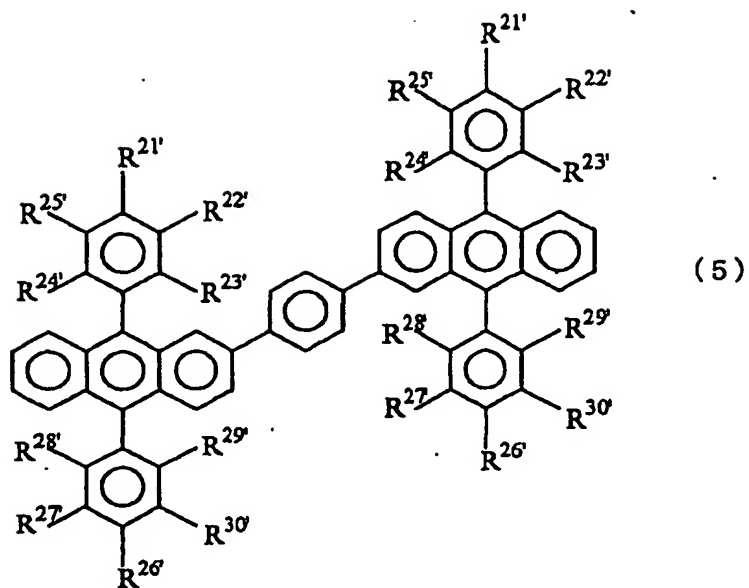
[0020] When the bis-condensed aromatic cyclic compound used in the present invention is comprised in the layer of organic compounds, the electric properties such as the driving voltage and the efficiency of light emission or the life of the device should not be affected by the bis-condensed aromatic cyclic compound but should remain the same as those of a device which does not comprise the compound. The bis-condensed aromatic cyclic compound is used to suppress crystallization in the device which may take place in driving for a long time or under change in the thermal environment. Therefore, it is preferable that the energy gap of the bis-condensed aromatic cyclic compound is the same as or greater than the energy gap of the light emitting material in the organic light emitting layer so that the bis-condensed aromatic cyclic compound does not take part in the recombination of electrons and holes or in the formation of the excited state. It is also preferable that the bis-condensed aromatic cyclic compound is a compound inactive to other compounds present in the organic light emitting layer. It is possible that the bis-condensed aromatic cyclic compound works supplementary for the electron transport and the hole transport.

[0021] When the bis-condensed aromatic cyclic compound is the compound represented by above general formula (2) and the light emitting material is the compound represented by above general formula (1), it is preferable that the energy gap of the compound represented by general formula (2) is greater than the energy gap of the compound represented by general formula (1).



[0022] Examples of the bis-condensed aromatic cyclic compound include compounds having structures represented by general formulae (4) to (6) shown in the following.



[0023] Examples of combinations of R^{21} to R^{30} in general formula (4) are shown in the following:



[0024] Examples of combinations of $R^{21'}$ to $R^{30'}$ in general formula (5) are shown in the following:

化合物 No.	R ³¹	R ³²	R ³³	R ³⁴	R ³⁵	R ³⁶	R ³⁷	R ³⁸	R ³⁹	R ⁴⁰
(6-1)	H	H	H	H	H	H	H	H	H	H
(6-2)	CH ₃	H	H	H	H	CH ₃	H	H	H	H
(6-3)	t-C ₄ H ₉	H	H	H	H	t-C ₄ H ₉	H	H	H	H
(6-4)	OCH ₃	H	H	H	H	OCH ₃	H	H	H	H
(6-5)	OPh	H	H	H	H	OPh	H	H	H	H
(6-6)	N(C ₂ H ₅) ₂	H	H	H	H	N(C ₂ H ₅) ₂	H	H	H	H
(6-7)	N(Ph) ₂	H	H	H	H	N(Ph) ₂	H	H	H	H
(6-8)	Ph	H	H	H	H	Ph	H	H	H	H
(6-9)		H	H	H	H		H	H	H	H
(6-10)	H	H	CH ₃	CH ₃	H	H	H	CH ₃	CH ₃	H
(6-11)	H	H	CH ₃	H	CH ₃	H	H	CH ₃	H	CH ₃
(6-12)	H	CH ₃	H	H	H	H	CH ₃	H	H	H
(6-13)	H	H	CH ₃	H	H	H	H	CH ₃	H	H
(6-14)	CH ₃	CH ₃	CH ₃	CH ₃	CH ₃	CH ₃	CH ₃	CH ₃	CH ₃	CH ₃

* Ph: Phenyl group

[0026] In the organic EL device of the present invention, it is preferable that the ratio of the amount by weight of the light emitting material to the amount by weight of the bis-condensed aromatic cyclic compound in the layer of organic compounds is in the range of 100:1 to 40:60 since the crystallization of the layer of organic compounds can be efficiently suppressed in driving the device for a long time or under change in the thermal environment without influence on the electric properties or the life of the device.

[0027] It is advantageous that the layer of organic compounds comprising the light emitting material and the bis-condensed aromatic cyclic compound in the above relative amounts is formed in accordance with the following process. The light emitting material and the bis-condensed aromatic cyclic compound are placed into separate boats for the source of vapor deposition and the vapor deposition is conducted while the relative rates of vapor deposition of the components are adjusted. Alternatively, the light emitting material and the bis-condensed aromatic cyclic compound are placed into the same boat for the source of vapor deposition in suitably adjusted relative amounts and the vapor deposition is conducted so that the layer of organic compounds comprising the light emitting material and the bis-condensed aromatic cyclic compound in the above relative amounts can be formed.

[0028] When the light emitting layer comprises the light emitting material and the bis-condensed aromatic cyclic compound, it is preferable that the film has a thickness of 5 nm to 0.5 μm since a device which exhibits a high efficiency and can be used under a low voltage is obtained.

[0029] The light emitting layer may further comprise a fluorescent molecule. Preferable examples of the fluorescent molecule include derivatives of styrylamine, distyrylamine, distyrylarylenes, coumarine, quinacridone, perylene, naphthalene and fluoranthene. By adding the fluorescent molecule into the light emitting layer, the organic EL device having a higher efficiency of light emission and a longer life can be obtained. More preferable examples of the fluorescent molecule include fluorescent molecules having a smaller energy gap than that of the light emitting material comprised

metal fluoride include LiF, Li₂O and NaF. As the process for forming the layer of an alkaline earth metal oxide, it is preferable that oxygen is introduced into an evacuated vessel under a vacuum adjusted to 10⁻³ to 10⁻⁴ Pa while the alkaline earth metal is vapor deposited in accordance with the vapor deposition process using resistance heating and the reaction of the alkaline earth metal with oxygen and deposition of the resultant oxide are simultaneously conducted.

The layer of an alkaline earth metal oxide can also be formed in accordance with the vapor deposition process using electron beams. As the process for forming the layer of an alkali metal oxide, the same process as that used for forming the layer of an alkaline earth metal oxide described above can be used. As the process for forming the layer of an alkali metal fluoride, the vapor deposition process using electron beams or the vapor deposition process using resistance heating can be used.

[0039] Embodiments of the process for preparing an organic EL device will be described with respect to the devices having various constructions. When the organic EL device has the construction of an anode / a light emitting layer / a cathode, a thin film made of a desired electrode material such as a material for the anode is formed on a suitable substrate in accordance with the vapor deposition process or the sputtering process so that the thickness of the formed thin film is 1 μm or smaller and preferably in the range of 10 to 200 nm. The formed thin film is used as the anode. On the formed anode, a thin film comprising the light emitting material and the bis-condensed aromatic cyclic compound is formed as the light emitting layer. For forming the thin film of the light emitting material, for example, the spin coating process, the casting process or the vapor deposition process may be used. The vapor deposition process is preferable since formation of pin holes can be suppressed.

[0040] When the light emitting layer is formed in accordance with the vapor deposition process, in general, it is preferable that the conditions are suitably selected in the following ranges: the heating temperature of the boat: 50 to 400°C; the vacuum: 10⁻⁵ to 10⁻³ Torr; the rate of deposition: 0.01 to 50 nm/second; the temperature of the substrate: -50 to +300°C and the thickness of the film: 5 nm to 5 μm; although the conditions of the vacuum vapor deposition are different depending on the organic compound used for the light emitting layer and the crystal structure and the association structure of the molecular deposition film to be formed. After the light emitting layer is formed, a thin film made of a material for the cathode is formed on the light emitting layer, for example, in accordance with the sputtering process so that the thickness of the formed thin film is 1 μm or smaller and preferably in the range of 50 to 200 nm. The formed film is used as the cathode and the desired organic EL device is obtained. The organic EL device may also be produced by forming the layers in the reverse order, i.e., in the order of the cathode, the light emitting layer and the anode.

[0041] When the device has a structure in which a layer of a mixture of a hole injecting and transporting material, a light emitting material and an electron injecting material is disposed between a pair of electrodes as the light emitting layer, a thin film of an anode material is formed on a suitable substrate. On the formed anode, a solution comprising the hole injecting and transporting material, the light emitting material, the bis-condensed aromatic cyclic compound, the electron injecting material and a binder such as polyvinylcarbazole is applied to the anode so that a film coating the anode is formed. A film may also be formed from the above solution in accordance with the dipping coating process. The formed film is used as the light emitting layer. A thin film of a cathode material is then formed on the light emitting layer. As another process, the light emitting material and the bis-condensed aromatic cyclic compound may be vapor deposited on the light emitting layer formed above and a film of a cathode material may be formed on the resultant layer. As still another process, the light emitting layer may be formed by simultaneous vapor deposition of the hole injecting and transporting material, the electron injecting material, the light emitting material and the bis-condensed aromatic cyclic compound and a film of a cathode material may be formed on the resultant layer.

[0042] When the organic EL device has a structure of an anode / a hole injecting and transporting layer / a light emitting layer / a cathode, the anode is formed at first in accordance with the same procedure as that described above. A thin film of a hole transfer compound is formed as the hole injecting and transporting layer in accordance with the spin coating process so that the hole injecting and transporting layer is formed. The conditions in the formation of the hole injecting and transporting layer is the same as those in the formation of the thin film of the light emitting material described above. The light emitting layer and the cathode are formed successively on the hole injecting and transporting layer in accordance with the same procedures as those described above and the desired organic EL device is obtained. The organic EL device may also be produced by forming the layers in the reverse order, i.e., in the order of the cathode, the light emitting layer, the hole injecting and transporting layer and the anode.

[0043] When the organic EL device has a structure of an anode / a hole injecting and transporting layer / a light emitting layer / an electron injecting layer / a cathode, the anode, the hole injecting and transporting layer and the light emitting layer are formed successively in accordance with the same procedures as those described above. A thin film of an electron transfer compound is formed on the light emitting layer in accordance with the spin coating process so that the electron injecting layer is formed. The cathode is formed on the electron injecting layer in accordance with the same procedures as those described above and the desired organic EL device is obtained.

[0044] The above organic EL device may also be produced by forming the layers in the reverse order, i.e., in the order of the cathode, the electron injecting layer, the light emitting layer, the hole injecting and transporting layer and the anode.

Example 2

[0052] An organic EL device was prepared in accordance with the same procedures as those conducted in Example 1 except that DPVDPAN as the light emitting material and bisanthracene compound (6-1) as the bis-condensed aromatic cyclic compound were binary vapor deposited in amounts such that the ratio of the amounts by weight was 49:51.

[0053] The properties of the prepared organic EL device were evaluated. When the anode of ITO was connected to the positive electrode (+) and the cathode of Al was connected to the negative electrode (-) and a direct current voltage of 6.78 V was applied, blue light was emitted at a luminance of 500 cd/m². The chromatic coordinates were (0.180, 0.290). When the device was sealed and driven under a constant current at an initial luminance of 500 cd/m² at a high temperature of 85°C, the change in the chromaticity was smaller than 0.01 after 200 hours. Thus, the chromaticity showed no change. The light emitting surface exhibited uniform light emission and the efficiency of light emission showed no decrease.

Example 3

[0054] An organic EL device was prepared in accordance with the same procedures as those conducted in Example 1 except that DPVDPAN as the light emitting material and bisanthracene compound (4-1) as the bis-condensed aromatic cyclic compound were binary vapor deposited in amounts such that the ratio of the amounts by weight was 49:51.

[0055] The properties of the prepared organic EL device were evaluated. When the anode of ITO was connected to the positive electrode (+) and the cathode of Al was connected to the negative electrode (-) and a direct current voltage of 6.87 V was applied, blue light was emitted at a luminance of 500 cd/m². The chromatic coordinates were (0.180, 0.318). When the device was sealed and driven under a constant current at an initial luminance of 500 cd/m² at a high temperature of 85°C, the change in the chromaticity was smaller than 0.01 after 200 hours. Thus, the chromaticity showed no change. The light emitting surface exhibited uniform light emission and the efficiency of light emission showed no decrease.

Example 4

[0056] An organic EL device was prepared in accordance with the same procedures as those conducted in Example 1 except that DPVDPAN as the light emitting material and bisanthracene compound (6-8) as the bis-condensed aromatic cyclic compound were binary vapor deposited in amounts such that the ratio of the amounts by weight was 90:10 and DMPAVB as the fluorescent molecule was not added.

[0057] The properties of the prepared organic EL device were evaluated. When the anode of ITO was connected to the positive electrode (+) and the cathode of Al was connected to the negative electrode (-) and a direct current voltage of 6.52 V was applied, blue light was emitted at a luminance of 225 cd/m². The chromatic coordinates were (0.152, 0.153). When the device was sealed and driven under a constant current at an initial luminance of 500 cd/m² at a high temperature of 85°C, the change in the chromaticity was smaller than 0.02 after 200 hours. Thus, the chromaticity showed no change. The light emitting surface exhibited uniform light emission and the efficiency of light emission showed no decrease.

[0058] In Examples 1 to 3 and Comparative Example 1, when the organic EL devices were driven under a constant current at an initial luminance of 500 cd/m² at a high temperature of 85°C, the half-life was 500 hours or longer. This value corresponds to 8,000 hours or longer when the devices were driven at the room temperature and the devices had the property sufficient for practical applications. Therefore, the bis-condensed aromatic cyclic compound showed no influence on the life of the organic EL devices.

[0059] In Example 4, when the organic EL device was driven under a constant current at an initial luminance of 500 cd/m² at a high temperature of 85°C, the half-life was 300 hours or longer. This value corresponds to 8,000 hours or longer when the device was driven at the room temperature at an initial luminance of 200 cd/m². Therefore, the crystallization was suppressed and uniform light emission was maintained.

INDUSTRIAL APPLICABILITY

[0060] In accordance with the present invention, the organic EL device which exhibits suppressed crystallization in driving for a long time or in environments at high temperatures, shows no change in the color of emitted light in use at high temperatures, has improved durability in that a uniform light emission is maintained and is advantageously used in practical applications can be obtained. The properties of the organic EL device such as the efficiency of light emission and the life are not adversely affected.

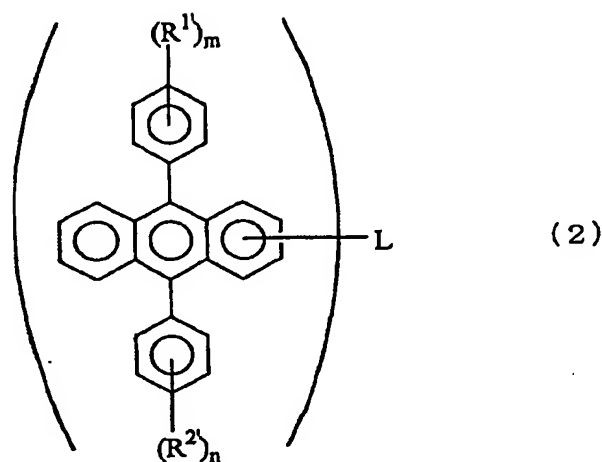
[0061] The organic EL device of the present invention can be advantageously used, for example, for displays of information instruments.

group having 6 to 30 carbon atoms, a substituted or unsubstituted amino group or a substituted or unsubstituted heterocyclic group having 2 to 30 carbon atoms and may represent a same group or different groups;

n and m each represent an integer of 0 to 5, when n represents an integer of 2 or greater, a plurality of R^1 may represent a same group or different groups and may be bonded to each other to form a cyclic structure and, when m represents an integer of 2 or greater, a plurality of R^2 may represent a same group or different groups and may be bonded to each other to form a cyclic structure; and

L represents a single bond, a substituted or unsubstituted arylene group having 6 to 30 carbon atoms, a substituted or unsubstituted alkylene group having 1 to 30 carbon atoms, -O-, -S- or -NR-, R representing a substituted or unsubstituted alkyl group having 1 to 30 carbon atoms or a substituted or unsubstituted aryl group having 6 to 30 carbon atoms.

7. An organic electroluminescence device according to Claim 5, wherein the bis-condensed aromatic cyclic compound is a compound represented by following general formula (2):



wherein R^1 and R^2 each independently represent a substituted or unsubstituted alkyl group having 1 to 30 carbon atoms, a substituted or unsubstituted cycloalkyl group having 5 to 30 carbon atoms, a substituted or unsubstituted aryl group having 6 to 30 carbon atoms, a substituted or unsubstituted alkenyl group having 3 to 30 carbon atoms, a substituted or unsubstituted alkoxy group having 1 to 30 carbon atoms, a substituted or unsubstituted aryloxy group having 6 to 30 carbon atoms, a substituted or unsubstituted amino group or a substituted or unsubstituted heterocyclic group having 2 to 30 carbon atoms and may represent a same group or different groups;

n and m each represent an integer of 0 to 5, when n represents an integer of 2 or greater, a plurality of R^1 may represent a same group or different groups and may be bonded to each other to form a cyclic structure and, when m represents an integer of 2 or greater, a plurality of R^2 may represent a same group or different groups and may be bonded to each other to form a cyclic structure; and

L represents a single bond, a substituted or unsubstituted arylene group having 6 to 30 carbon atoms, a substituted or unsubstituted alkylene group having 1 to 30 carbon atoms, -O-, -S- or -NR-, R representing a substituted or unsubstituted alkyl group having 1 to 30 carbon atoms or a substituted or unsubstituted aryl group having 6 to 30 carbon atoms.

8. An organic electroluminescence device according to Claim 1, wherein the bis-condensed aromatic cyclic compound is a compound represented by following general formula (3):

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP01/10273

A. CLASSIFICATION OF SUBJECT MATTER Int.Cl. ⁷ H05B 33/14, C09K 11/06		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) Int.Cl. ⁷ H05B 33/00-33/28		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Jitsuyo Shinan Koho 1940-1996 Toroku Jitsuyo Shinan Koho 1994-2001 Kokai Jitsuyo Shinan Koho 1971-2001 Jitsuyo Shinan Toroku Koho 1996-2001		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP 2000-208264 A (Idemitsu Kosan Co., Ltd.), 28 July, 2000 (28.07.00), Full text; all drawings (Family: none)	1-11
Y	JP 8-12600 A (TDK Corporation), 16 January, 1996 (16.01.96), Full text; all drawings & DE 69511755 C & EP 681019 A2 & US 5635308 A1	1-11
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
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Date of the actual completion of the international search 11 December, 2001 (11.12.01)		Date of mailing of the international search report 25 December, 2001 (25.12.01)
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